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# **Aerobic degradation potential of the herbicides mecoprop, dichlorprop and bentazone in groundwater from chalk aquifers**

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## **Abstract**

The aerobic degradation potential of mecoprop, dichlorprop and bentazone was studied at concentration of 1 µg/L in laboratory batch experiments with groundwater from chalk aquifers. Within the incubation period of 129 days, <sup>14</sup>C-mecoprop concentration decreased to 60-80% in the microcosms with groundwater collected from two monitoring wells (Well 1 and 2). Dichlorprop degradation was neither observed under aerobic nor anaerobic conditions, while 17-27% of the initial concentration of <sup>14</sup>C-bentazone was removed. The results indicated a degradation potential of mecoprop and bentazone under aerobic conditions.

## **Introduction**

Organic micro pollutants such as pesticides and degradation products are detected in an increasing number of aquifers all over the world (Barbash et al., 2001). In some countries such as Denmark, drinking water supply is based on groundwater, treated with a simple aeration and filtration process before it is distributed directly to the consumers. This requires high quality groundwater that must meet the standards in EU Groundwater directive with threshold limit values for pesticides and their metabolites in groundwater at 0.1 µg/L for each pesticide or metabolite and 0.5 µg/L for the sum of pesticides and metabolites (European Parliament and Council, 2006). The frequent findings of pesticides in Danish groundwater have resulted in the closure of many drinking water wells. In the period 1987-2007 a total of 2176 Danish abstraction wells were closed, 25% of these due to pesticide contamination (Miljøstyrelsen, 2009). Diffuse pesticide pollution is one of the major environmental challenges since it is difficult to remediate aquifers contaminated with trace concentrations.

The natural redox conditions of aquifers are considered to be one of the important factors governing the degradation of pesticides in groundwater (Larsen et al, 2001). In and around drinking water abstraction fields the geological structure may be complex with dual porosity which in combination with changing abstraction patterns may lead to mixing of different water types, creating steep concentration gradients and drastic redox changes. This may stimulate microbial degradation of the contaminants by addition of relatively low oxygen concentrations (Tuxen et al., 2006). Therefore, geological variations in combination with water abstraction may affect microbial degradation processes and redox conditions in aquifers (Ludvigsen et al., 1998; Janniche et al., 2011).

The present investigation focused on three pesticides; mecoprop, dichlorprop and bentazone which are some of the most frequently found and detected pesticides in Danish groundwater. The selected pesticides are all herbicides and are moderately soluble in water and include both non-polar compounds and dissociable compounds. The purpose of the study was to examine the aerobic degradation potential of three pesticides in slightly pesticide contaminated groundwater from chalk aquifers.

## **Materials and Methods**

### **Groundwater sampling**

Groundwater samples were collected from two monitoring and three drinking water wells approximately 1 m above the screen in February 2010 and wells were purged three volumes before sampling. The drinking water wells were owned by the major water supply of Denmark, København Energi, KE. Oxygen, pH, temperature and electrical conductivity were measured in the field with a flow cell. Groundwater samples for pesticide mineralization experiments were collected in 1L sterilized glass bottles with overflow in order to prevent aerobic conditions and kept at 10°C until setting up the experiments.

### **Mineralization investigations**

Pesticide mineralization investigations were performed with [ring-<sup>14</sup>C]-mecoprop (Izotop, Budapest, Hungary, 95% radiochemical purity, 23mCi/mmol), [ring-<sup>14</sup>C]-dichlorprop (Izotop, Budapest, Hungary, 99.03% radiochemical purity, 25mCi/mmol) and [carbonyl-<sup>14</sup>C]-bentazone (Izotop, Budapest, Hungary, 97.96% radiochemical purity, 44mCi/mmol). Aerobic incubations were set up for each pesticide in duplicates and incubated in the dark at 10°C, corresponding to the aquifer temperature. Each bottle had a headspace of atmospheric air. Control incubations for biological activity, were autoclaved 20 minutes at 1.5 bars and 120°C at three times with one day intervals. For dichlorprop 6 anaerobic incubation bottles were set up in where the headspace were replaced with 80% N<sub>2</sub>/20% CO<sub>2</sub>-gas mixture in order to remove all oxygen.

Laboratory batch experiments contained 40g autoclaved chalk sediment and 60mL groundwater in 100 mL DURAN bottles with Teflon inlayer caps for aerobic incubations. <sup>14</sup>C-ring labelled dichlorprop, mecoprop and bentazone were added to a concentration of 1µg/L of pesticide to each of the bottles. For <sup>14</sup>C- activity measurements, 2mL water subsamples were collected at each sampling and transferred to a 20 mL polyethylene scintillation vial containing a 6 mL scintillation vial with 1 mL 0.5 M NaOH. The subsample was acidified by adding 0.1 mL 37% HCl to strip off <sup>14</sup>CO<sub>2</sub>. The 6 mL inner vial of this 'double vial' system served as a CO<sub>2</sub> trap and was removed after 48 hours. Scintillation liquid was added and the <sup>14</sup>C-activity of both the 20 mL vial and the 6 mL vial was quantified by counting for 20 minutes in a liquid scintillation analyser.

## **Results and Discussion**

### **Groundwater characterization**

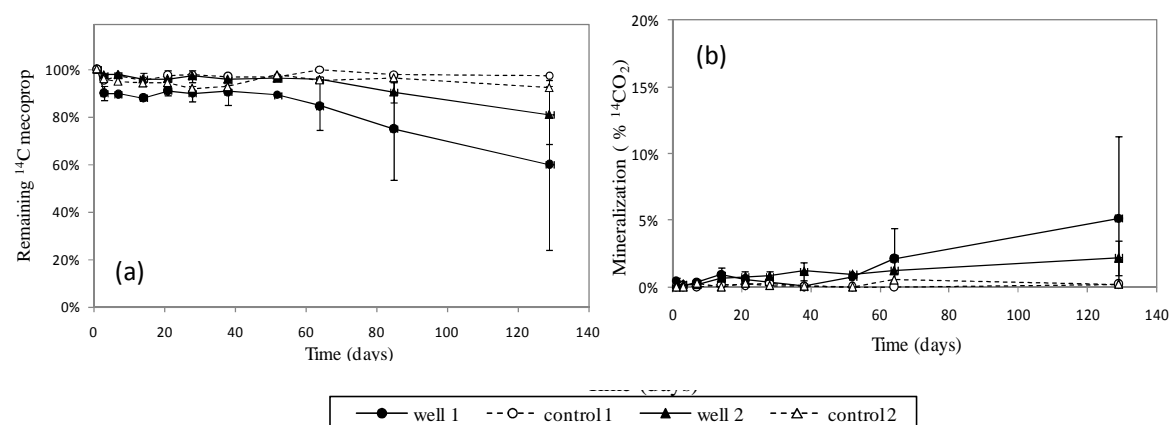
The collected groundwater was in the neutral range (pH 7.1-7.4) and anaerobic, indicating reduced conditions ranging from nitrate reducing to iron reducing in all five wells (Table 1). Water from Well 1 (screened 28-30 meter below surface (mbs)) had the highest oxygen concentration and microbial activity. Well 2 had the highest concentrations of sulphate, chloride, magnesium, calcium, sodium and methane. Well 2, 3, and 4 had the lowest concentrations of Fe (II). Well 3 had the highest concentration of nitrate, but lowest sulphate concentration. The water samples from wells 2-5 represented a relatively long depth interval and they were thus not as depth-specific as the water sampled from well 1.

**Table 1: Characterization of groundwater from the five sampled wells**

	Well 1	Well 2	Well 3	Well 4	Well 5
Screen depth (mbs)	28-30	9-24	14-35	14-35	16.5-28.5
Temperature (°C)	4.0	9.5	9.1	9.0	9.1
pH	7.37	7.05	7.15	7.05	7.12
Conductivity ( $\mu\text{S}/\text{cm}$ )	420	666	540	489	599
Oxygen (mg/L)	0.35	0.06	0.11	0.22	0.03
$\text{Cl}^-$ (mg/L)	34.1	52.7	44.0	35.1	34.3
$\text{Mg}^{2+}$ (mg/L)	25.3	24.2	22.7	22.0	22.1
$\text{Ca}^{2+}$ (mg/L)	120.3	183.6	136.9	142.8	160.8
$\text{Na}^+$ (mg/L)	20.0	21.3	18.3	15.4	15.9
$\text{K}^+$ (mg/L)	3.22	9.3	3.67	3.02	3.89
$\text{Mn}^{2+}$ (mg/L)	0.034	0.053	0.039	0.034	0.059
$\text{CH}_4$ (mg/L)	0.257	0.007	0.019	0.012	0.010
$\text{SO}_4^{2-}$ (mg S/L)	178	192	141	183	181
$\text{Fe}^{2+}$ (mg/L)	2.02	0.63	0.69	0.52	2.48
$\text{NO}_3^-$ (mg N/L)	0.08	0.04	2.17	0.44	0.02
$\text{NH}_4^+$ (mg N/L)	0.57	2.48	0.38	0.18	0.31
Dissolved Organic Carbon (mg/L)	1.832	2.592	1.851	1.726	1.858
ATP (pg/mL)	58.0	16.9	23.4	2.8	6.7

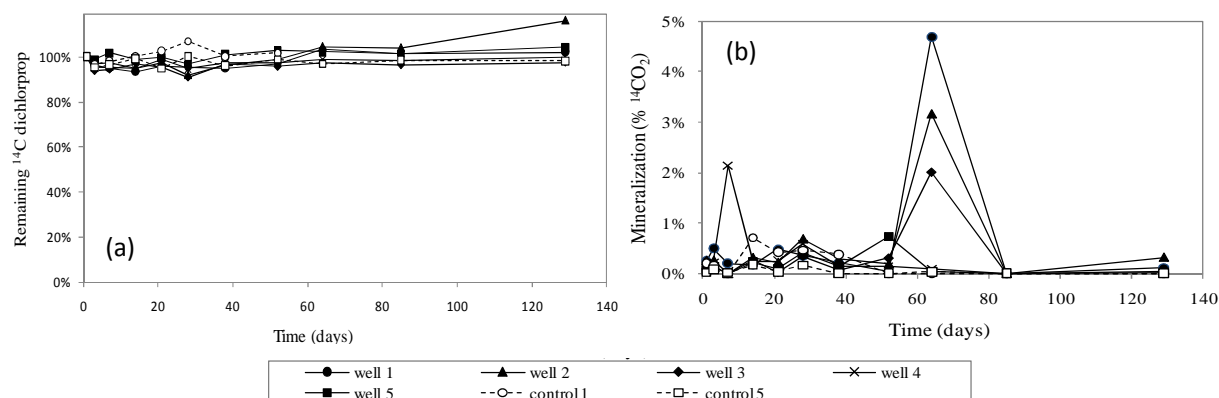
### Mineralization potential

Mecoprop concentration in the laboratory experiments with water collected from Well 1 and Well 2 decreased to approximately 60-80% of the initial concentration under aerobic conditions, while 92-97% was remained in the autoclaved controls after 129 days incubation. After a long lag phase, significant decrease of mecoprop was noted in well 1 (Figure 1). Mineralization was slow, but the  $^{14}\text{CO}_2$  production was substantially higher (2-5%) than the level in the autoclaved controls (0.0-0.5%). The observed degradation potential of mecoprop is in accordance with previous investigations involving chalk under aerobic conditions (Janniche et al., 2010, Kristensen et al., 2001), though their studies revealed slightly shorter lag phases and indicated a potential degradation under aerobic conditions.



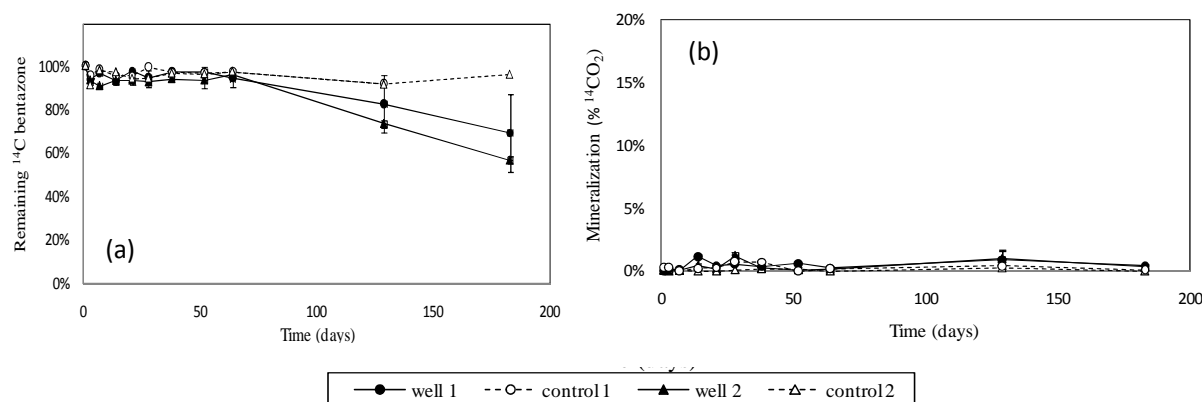
**Figure 1:** Degradation of mecoprop under aerobic conditions. (a) Remaining pesticide, (b) mineralization (relative  $^{14}\text{CO}_2$  production)

Dichlorprop degradation was neither observed under aerobic nor anaerobic conditions within the incubation period of 129 days. 97-104% of the initial dichlorprop concentration remained under aerobic condition (Figure 2). Studies by Pedersen (2000) and de Liphay et al., (2000) showed recalcitrance of dichlorprop under aerobic conditions. In contrast, degradation of dichlorprop was observed in a laboratory column experiment (Tuxen et al. 2000) and a continuous field injection experiment (Broholm et al. 2001) in an aerobic aquifer.



**Figure 2:** Degradation of dichlorprop under aerobic conditions. (a) Remaining pesticide, (b) mineralization (relative  $^{14}\text{CO}_2$  production)

For bentazone 17-27% of the initial concentration was removed after 129 days of incubation, while only 9% was removed in the abiotic controls (Figure 3). Though bentazone usually is considered to be recalcitrant (Tuxen et al., 2002 and Broholm et al., 2001), a degradation potential for bentazone in groundwater was observed.



**Figure 3:** Degradation of bentazone under aerobic conditions. (a) Remaining pesticide, (b) mineralization (relative  $^{14}\text{CO}_2$  production)

Tuxen et al. (2006) investigated how increasing oxygen concentrations affected the length of lag phase and degradation rate. Mecoprop mineralization was then higher (53 %) with high oxygen concentration compared to the one (32 %) with low oxygen concentration and the length of the lag phase was shortened 10 times in the microcosm experiments with high oxygen concentration (7.7 mg/L) compared with low oxygen concentration (<0.3 mg/L).

## Conclusion

Batch experiments with chalk material and groundwater showed degradation potential for mecoprop and bentazone in presence of oxygen. To our knowledge, bentazone has not been reported before to

be degraded with aquifer material. In order to gain more knowledge regarding to bentazone degradation in aquifer material, optimization of redox conditions from anaerobic to aerobic by adding oxygen concentration must be studied.

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